

Predicted Effects of Mineral Neutralization and Bisulfate Formation on Hydrogen Ion Concentration for Dilute Sulfuric Acid Pretreatment

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Abstract

Dilute acid and water-only hemicellulose hydrolysis are being examined as part of a multiinstitutional cooperative effort to evaluate the performance of leading cellulosic biomass pretreatment technologies on a common basis. Cellulosic biomass, such as agricultural residues and forest wastes, can have a significant mineral content. It has been shown that these minerals neutralize some of the acid during dilute acid pretreatment, reducing its effectiveness, and the higher solids loadings desired to minimize costs will require increased acid use to compensate. However, for sulfuric acid in particular, an equilibrium shift to formation of bisulfate during neutralization can further reduce hydrogen ion concentrations and compound the effect of neutralization. Because the equilibrium shift has a more pronounced effect at lower acid concentrations, additional acid is needed to compensate. Coupled with the effect of temperature on acid dissociation, these effects increase acid requirements to achieve a particular reaction rate unless minerals are removed prior to hydrolysis.

Index Entries: Pretreatment; dilute acid; hemicellulose hydrolysis; bisulfate; neutralization.

Introduction

Cellulose ethanol has the potential to displace a significant amount of petroleum in the United States, reducing the nation's dependence on foreign imports (1). The biologic processes favored for producing ethanol from lignocellulosic biomass require a pretreatment step before high yields can be realized, and the accessibility of cellulose to cellulase enzymes has

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been shown to increase with removal of hemicellulose (2). Furthermore, the addition of dilute acid accelerates the breakdown of hemicellulose through the generation of greater concentrations of hydrogen ions and also improves recovery of hemicellulose sugars for later fermentation to ethanol and other products (3). Although many different acids have been used in dilute-acid pretreatment including nitric and hydrochloric, sulfuric acid is often favored because of its low cost (4), but pretreatment is still among the most costly steps in a biomass-to-fuels-and-chemicals process (5,6).

When considered for process design, several factors are responsible for the high capital and operating costs of dilute-acid pretreatment processes. First, dilute sulfuric acid requires expensive materials for construction. Second, the high temperatures used result in high pressures and compound containment costs. Third, feeding solid materials to high pressure operations is costly, and substantial energy is required to heat up the biomass to pretreatment temperatures. Finally, although sulfuric acid is relatively low in cost, the quantities required are substantial, and additional costs are incurred for neutralization and conditioning chemicals prior to cellulose hydrolysis and hydrolysate fermentation as well as disposal of neutralization products.

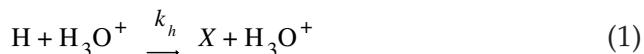
Overall, these factors suggest that it would be desirable to reduce acid use and the severity of the reaction conditions if the costs of hemicellulose hydrolysis by pretreatment are to be reduced. Kinetic models could provide some insight into tradeoffs between acid consumption and yields, and a review by Jacobsen and Wyman (7) describes how acid has been incorporated into previous hemicellulose hydrolysis models. Most of these models include acid concentration but on a mass basis (8). Several include acid neutralization by minerals in biomass (9). Because the acid dissociation constant is a function of temperature, it has also been shown that the concentration of active hydrogen ion decreases with pretreatment temperature for sulfuric acid (10). For example, Springer and Harris (11), as well as others, raise the acid concentration to an empirical power apparently as a means of accounting for these effects. Unfortunately, although such models can describe the data from which they were derived, there can be inconsistencies among studies using the same substrate, limiting their utility for tuning acid concentration while maintaining acceptable yields.

Experimental results in the literature for many sulfuric acid-catalyzed pretreatment studies with a variety of feedstocks show that hemicellulose sugar recovery increases with acid addition, at least initially, and some acid is desirable to achieve high sugar yields from pretreatment and subsequent enzymatic hydrolysis of cellulose (12–15). In addition, previous studies have shown that minerals in biomass can neutralize some of the added acid, increasing acid demand to reach a pH targeted for high yields (13). A third effect not previously reported for hemicellulose hydrolysis is that neutralization of sulfuric acid forms bisulfates that also reduce the hydrogen ion concentration (increase pH) (16). Thus, the present study was directed toward understanding how acid concentra-

tion, temperature, and the coupled effects of sulfuric acid neutralization by minerals and bisulfate formation could interplay and impact hemicellulose hydrolysis.

Predicting Catalytic Effect of Acid on Hemicellulose Hydrolysis

It is often assumed that hemicellulose hydrolysis is a first-order homogeneous reaction in hemicellulose, that is



in which H is hemicellulose, H_3O^+ is the hydronium ion, and X is xylose.

A typical model applies a rate constant of the form

$$k_h = Ae^{-E/RT} \quad (2)$$

in which the preexponential factor A is a function of acid concentration, but the activation energy E is considered independent of temperature and acid concentration. This expression can be rewritten to explicitly include the effect of acid concentration:

$$A = A_0C^m \quad (3)$$

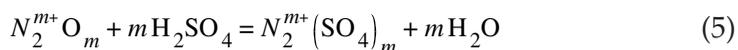
in which C is the acid concentration in percent added prior to hydrolysis, and m is an arbitrary constant that varies with the type of biomass being pretreated. Equations 2 and 3 can be combined to give

$$k_h = A_0C^m e^{-E/RT} \quad (4)$$

Typical values of m of between about 0.4 and 1.6 have been reported in the literature (13). The use of percent acid in this expression appears to be arbitrary. Other investigators have used normality or molarity of the added acid, and yet others have used the pH taken at room temperature after hydrolysis. This arbitrary use of the acid concentration may explain why the power term m and the kinetic rate constants vary so widely, even for investigations using the same substrate, underscoring the need for consistent use of this term.

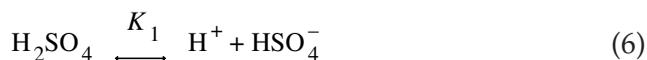
Effect of Acid Neutralization

Both Eqs. 3 and 4 show that hydrogen ion concentration should affect the rate of hemicellulose hydrolysis, but the neutralization capacity of biomass is not always taken into consideration in models reported in the literature. Neutralization is caused by basic minerals containing potassium, sodium, calcium, iron, and other cations present in biomass reacting with sulfuric acid and reducing available hydrogen ions stoichiometrically (17):



in which N^{m+} is the cation and m is its valence. Because mineral content varies from species to species, neutralization capacity must be determined

experimentally, although it may be possible to correlate neutralization capacity from mineral analyses. In a dry method described in Tappi standard method T-211 (18) a biomass sample is ashed, and the ash is neutralized with an excess of sulfuric acid, which is backtitrated with sodium hydroxide. To understand how neutralization by minerals impacts hydrogen ion concentration, one starts with dissociation of sulfuric acid as described by the following coupled equations:



From this, the equilibrium concentrations of each species can be predicted from the dissociation constants K_1 and K_2 as follows:

$$K_1 = \frac{[\text{H}^+][\text{HSO}_4^-]}{[\text{H}_2\text{SO}_4]} \quad (8)$$

$$K_2 = \frac{[\text{H}^+][\text{SO}_4^{=}]}{[\text{HSO}_4^-]} \quad (9)$$

Assuming K_1 to be large (i.e., the first dissociation reaction is essentially complete), then the total hydrogen ion concentration is primarily affected by the second dissociation reaction, and Eq. 9 can be rearranged to

$$[\text{SO}_4^{=}] = K_2 \frac{[\text{HSO}_4^-]}{[\text{H}^+]} \quad (10)$$

When partial neutralization of added sulfuric acid occurs because of minerals in the biomass, a sulfate imbalance occurs: some of the hydrogen ion is converted to water and some sulfate is then associated with mineral cations (Eq. 5). That is, for every equivalent of sulfuric acid neutralized, an equivalent amount of sulfate ions associated with mineral cations is created. The sulfate imbalance is equal to the number of moles of sulfuric acid neutralized, and if one lets M = concentration of sulfuric acid remaining after neutralization and N = sulfate concentration resulting from neutralization, then the sulfate balance can be expressed as follows:

$$[\text{HSO}_4^-] + \text{SO}_4^{=} - M - N = 0 \quad (11)$$

Substituting the expression for $[\text{SO}_4^{=}]$ from Eq. 10 into Eq. 11, one obtains

$$[\text{HSO}_4^-] + K_2 \frac{[\text{HSO}_4^-]}{[\text{H}^+]} - M - N = 0 \quad (12)$$

The charge balance can be expressed as

$$[\text{H}^+] + 2N - [\text{HSO}_4^-] - 2[\text{SO}_4^{2-}] = 0 \quad (13)$$

or

$$[\text{H}^+] + 2N - [\text{HSO}_4^-] - 2K_2 \frac{[\text{HSO}_4^-]}{[\text{H}^+]} = 0 \quad (14)$$

Then from the sulfate balance (Eq. 12) one can obtain

$$[\text{HSO}_4^-] = \frac{[\text{H}^+](M + N)}{[\text{H}^+] + K_2} \quad (15)$$

Substituting this result into the charge balance (Eq. 14) and eliminating $[\text{HSO}_4^-]$, the following quadratic equation results:

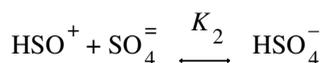
$$[\text{H}^+]^2 + (K_2 + M - N)[\text{H}^+] - 2K_2M = 0 \quad (16)$$

Solving for $[\text{H}^+]$ leads to

$$[\text{H}^+] = \frac{-(K_2 + M - N) + \sqrt{(K_2 + M - N)^2 + 8K_2M}}{2} \quad (17)$$

Effect of Sulfate on Hydrogen Ion Activity

A second effect on hydrogen ion activity not previously considered in dilute-acid hydrolysis of hemicellulose is the shift to bisulfate that occurs with neutralization. Neutralization products are water and mineral sulfates (Eq. 5). These mineral sulfates, if not removed from the system, will form bisulfates from some of the remaining hydronium ions to reestablish equilibrium as follows (Eq. 7):



This further reduces the hydronium ion concentration, and this effect is even greater at elevated temperatures because the equilibrium constant decreases.

Effect of Temperature on Hydrogen Ion Activity

Equation (17) can predict the hydrogen ion activity for dilute sulfuric acid solutions containing neutralization salts with a concentration of N mol/L at a standard temperature such as 25°C for which dissociation constants have been tabulated. However, modifications are required to predict the hydrogen ion activity at elevated temperatures of about 100°C to >200°C, typical for hemicellulose hydrolysis. Increasing temperature accelerates rates via an Arrhenius effect but also affects the activity of hydrogen ions, i.e., the effective ion concentration after accounting for solution nonidealities. Although a pH meter measures hydrogen ion activity, it is

difficult if not impossible to measure pH reliably above about 100°C, and hydrogen ion activity generally must be estimated for higher temperatures. In this case, the solution dissociation constant K_2 in Eq. 17 is related to the thermodynamic dissociation constant K_2^0 (solution dissociation constant extrapolated to infinite dilution) by

$$K_2^0 = \frac{a_{\text{H}^+} a_{\text{SO}_4^{2-}}}{a_{\text{HSO}_4^-}} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} \frac{\gamma_{\text{H}^+} \gamma_{\text{SO}_4^{2-}}}{\gamma_{\text{HSO}_4^-}} = K_2 \frac{\gamma_{\text{H}^+} \gamma_{\text{SO}_4^{2-}}}{\gamma_{\text{HSO}_4^-}} \quad (18)$$

$$K_2 = K_2^0 \frac{\gamma_{\text{HSO}_4^-}}{\gamma_{\text{H}^+} \gamma_{\text{SO}_4^{2-}}} \quad (19)$$

in which a_i is the ionic activity (mol/L), and γ_i is the ionic activity coefficient. The relation developed by Marshall from experiments determining the solubility of calcium sulfate in sulfuric acid solutions at elevated temperatures can then be used to estimate the values of the thermodynamic dissociation constant, K_2^0 , as a function of temperature (19):

$$\text{Log } K_2^0 = 56.889 - 19.8858 \text{ Log } T - 2307.9/T - 0.006473T \quad (20)$$

in which T is the temperature in Kelvin. For the activity coefficients γ_i , we used an empirical correlation by Davies (20), which is a modification of the Debye-Hückel limiting law:

$$-\text{Log } \gamma_i = Az^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) \quad (21)$$

in which I is the ionic strength $\frac{1}{2} \sum n_i z_i^2$; γ_i is the ionic activity coefficient; A is the Debye-Hückel constant $= 1.825 \times 10^6 (\epsilon T)^{-1.5}$; ϵ is the dielectric constant of water $= 132.88 - .208T$; z is the ionic charge; n is the ion molarity; and T is the temperature (K). Assuming that the two monovalent activity coefficients are equal, the expression for the solution dissociation constant after rearranging Eq. 19 becomes

$$K_2 = \frac{K_2^0}{\gamma_{\text{SO}_4^{2-}}} \quad (22)$$

By substituting this result into Eq. 17 and remembering that the activity of the hydrogen ion $a_{\text{H}^+} = [\text{H}^+] \gamma_{\text{H}^+}$ (in which a_{H^+} is in mol/L) one now has

$$a_{\text{H}^+} = \left\{ - \left(\frac{K_2^0}{\gamma_{\text{SO}_4^{2-}}} + M - N \right) + \left[\left(\frac{K_2^0}{\gamma_{\text{SO}_4^{2-}}} + m - n \right)^2 + 8 \frac{K_2^0}{\gamma_{\text{SO}_4^{2-}}} M \right]^{1/2} \right\} \frac{\gamma_{\text{H}^+}}{2} \quad (23)$$

This expression predicts the hydrogen ion activity for any concentration of neutralization products and at any temperature. By inserting this result in the kinetic rate expression of Eq. 4 in place of the acid term, one obtains:

$$k_h = A_0 a_{\text{H}^+} e^{-E/RT} \quad (24)$$

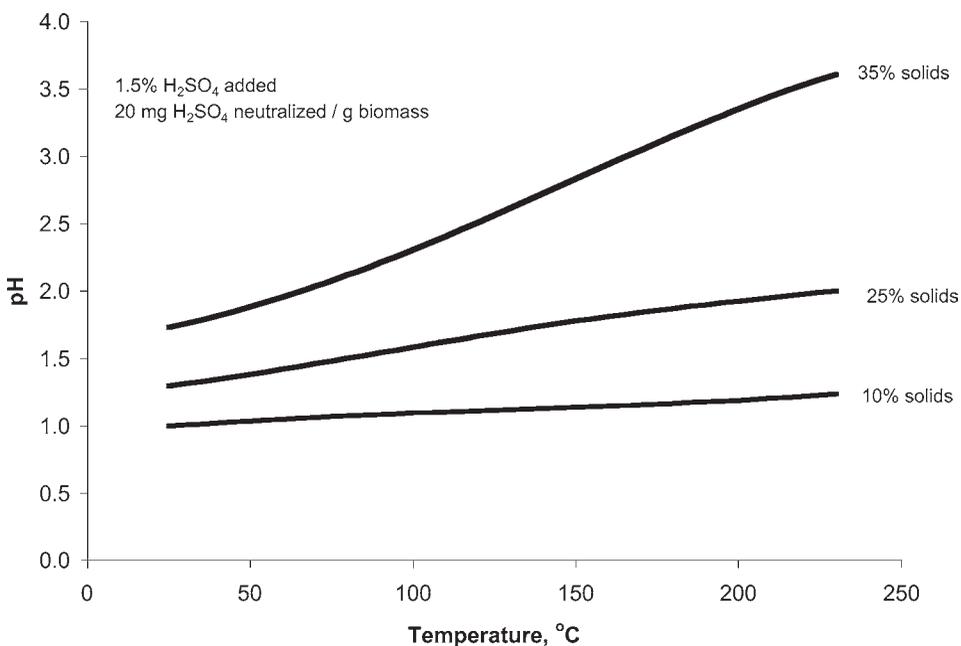


Fig. 1. Change in pH with temperature and solids loadings for solution originally containing 1.5% H₂SO₄ (w/w).

To make Eq. 24 dimensionally consistent with Eq. 4, one can convert a_{H^+} to mole fraction from molarity by dividing by the overall mole density of solution (also a function of temperature). One now has an expression that includes the effect of temperature and neutralization on added acid and can be used to predict pretreatment hydrolysis performance.

Combined Effects of Neutralization, Sulfate, and Temperature

To illustrate how acid neutralization, sulfate formation, and temperature could potentially affect hemicellulose hydrolysis, suppose several different concentrations of biomass solids were added to a 1.5% H₂SO₄ solution and treated over a temperature range of 25–160°C. Further assume that 20 mg of sulfuric acid is neutralized per g of dry biomass, and pH, defined as $\text{pH} = -\text{Log}_{10} a_{\text{H}^+}$ is taken as the measure of hydrogen ion concentration. For this case, Fig. 1 illustrates how pH would vary with temperature based on Eq. 24 at 10, 25% and 35% solids concentrations and hence three different neutralization product (sulfate salt) concentrations. A sharp rise in pH with increasing temperature in the presence of neutralization products occurs owing to an equilibrium shift of the hydrogen ion to bisulfate ion via Eq. 8 and the impact of temperature on hydrogen ion activity via Eq. 24. Furthermore, this effect is magnified with increasing temperature, and the pH rises about 0.15 units for a solids loading of 10%

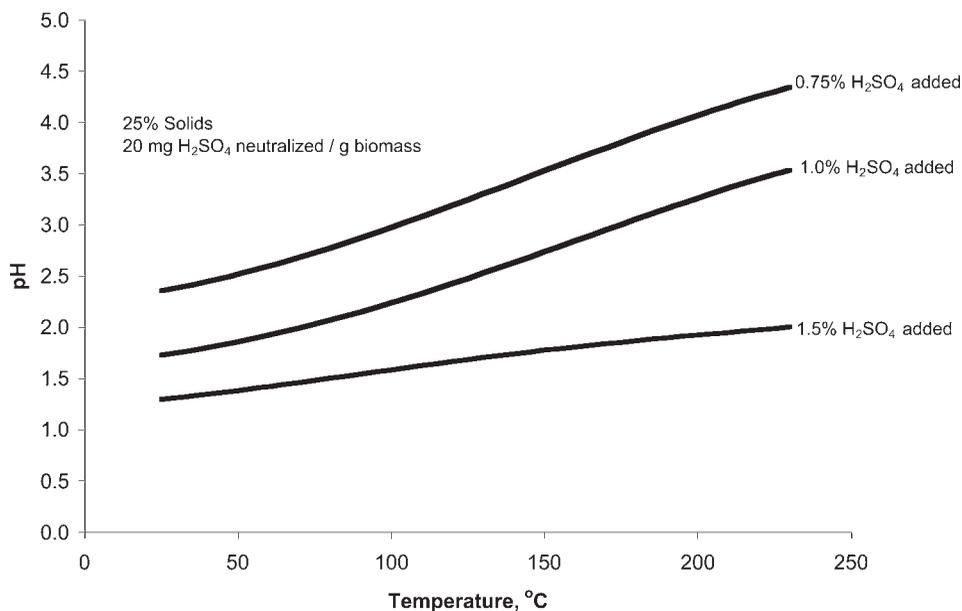


Fig. 2. Effect of acid concentration on pH as function of temperature for three different initial H₂SO₄ concentrations assuming 25% solids and 20 mg of acid/g of biomass neutralization capacity.

and about 1.2 units for a solids loading of 35%, corresponding to about a 29 and a 94% reduction in hydrogen ion activity, respectively. By contrast, if there had been no neutralization, the pH would rise just 0.11 units, from 0.89 to 1.00, over the same temperature range regardless of solids loading corresponding to a 22% reduction in hydronium ion activity.

Figure 2 shows the effect of initial acid concentration again assuming that 20 mg of sulfuric acid is neutralized/g of dry biomass and 25% solids loading. As the ratio of neutralization products to sulfuric acid increases (added acid is decreased), pH becomes increasingly temperature dependent. As an example of this effect, consider a batch pretreatment at 25% solids performed at 160°C. Adding a sulfuric acid solution with an initial concentration of 1.5% (w/w) before 20 mg/g of biomass neutralization occurs, and assuming that neutralization products are not removed, the pH shown in Fig. 2 is 1.81. Intuitively, one would expect that cutting the acid concentration in half would also cut the hydrogen ion activity in half, but Fig. 2 shows that a pH of 3.64 would be obtained for an initial sulfuric acid concentration of 0.75% at 160°C, a reduction of >98% rather than the 50% level one might expect. By contrast, if there had been no neutralization, reducing the acid addition from 1.5 to 0.75% at 160°C would result in the pH rising from 1.00 to 1.26, corresponding to a 45% reduction in hydronium ion. This is somewhat less than the 50% expected owing to the favorable equilibrium shift to the hydronium ion.

Conclusion

Neutralization of sulfuric acid by the minerals in biomass reduces the hydrogen ion activity and must be taken into account for models to accurately predict the performance of dilute-acid hemicellulose hydrolysis. Furthermore, in the case of sulfuric acid, the neutralization products lead to a bisulfate ion shift, further reducing active hydrogen ion. Neutralization and formation of bisulfate can have particularly significant effects for low acid concentrations or high solids loadings. Thus, it may be worthwhile to remove minerals or neutralization products prior to hydrolysis if one wishes to reduce acid consumption for hemicellulose hydrolysis while maintaining high sugar yields. Further experiments are required to validate the predicted effects of mineral neutralization, bisulfate formation, and temperature on dilute-acid pretreatment of biomass.

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References

1. Wyman, C. E. (1999), *Annu. Rev. Energy Environ.* **24**, 189–226.
2. Torget, R., Hatzis, C., Hayward, T. K., Hsu, T.-A., and Philippidis, G. D. (1996), *Appl. Biochem. Biotechnol.* **57/58**, 85–101.
3. Allen, G. A., Schulman, D., Lichwa, J., and Antal, Jr., M. J. (2001), *Ind. Eng. Chem. Res.* **40**, 2352–2361.
4. Hsu, T. A., Himmel, M., Schell, D., Farmer, J., and Berggren, M. (1996), *Appl. Biochem. Biotechnol.* **57/58**, 3–18.
5. Wooley, R. Ruth, M., Glassner, D., and Sheehan, J. (1999), *Biotechnol. Prog.* **15**, 794–803.
6. Lynd, L. R., Elander R. T., Wyman C. E. (1996). *Appl. Biochem. Biotechnol.* **57/58**, 741–761.
7. Jacobsen, S. E., and Wyman, C. E. (2000), *Appl. Biochem. Biotechnol.* **84-86**, 81–95.
8. Belkacemi, N., Abatzoglou, N., Overend, R. P., and Chornet, E. (1991), *Ind. Eng. Chem. Res.* **30**, 2416–2425.
9. Maloney, M. T. and Chapman, T. W. (1985), *Biotechnol. Bioeng.* **27**, 355–361.
10. Adamson, A. W. (1973), *A Textbook of Physical Chemistry*, Academic, New York, NY.
11. Springer, E. L., Harris, and J. F. (1985), *Ind. Eng. Chem. Prod. Res. Dev.* **24**, 485–489.
12. Grethlein, H. E., Allen, D. C., and Converse, A. O. (1984), *Biotechnol. Bioeng.* **26**, 1498–1505.
13. Esteghlalian, A., Hashimoto, A. G., Fenske, J. J., and Penner, M. H. (1997), *Bioresour. Technol.* **59**, 129–136.
14. Torget, R. and Hsu, A. T. (1994), *Appl. Biochem. Biotechnol.* **45/46**, 5–21.
15. Bhandari, N., MacDonald, D. G., and Bakhshi, N. N. (1984), *Biotech. Bioeng.* **26**, 320–327.
16. Readnour, J. M. and Cobble, J. W. (1969), *Inorg. Chem.* **8(10)**, 2174–2182.
17. BeMiller, J. N. (1967), *Adv. Carbohydr. Chem.* **22**, 25–108.

18. TAPPI. (2002), Ash in wood, pulp, paper and paperboard: combustion at 525°C, in *Documenty number TAPPI T-211*, Technical Association of the Pulp and Paper Industry, Norcross, GA.
19. Marshall, W. L. and Jones, E. V. (1966), *J. Phys. Chem.* **70/12**, 4028–4040.
20. Davies, C. W. (1930), *The Conductivity of Solutions and the Modern Dissociation Theory*, J. Wiley & Sons, New York, NY.